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(54) **Method for the production of aliphatic copolyester films.**

(57) There is disclosed a method for the production of aliphatic copolyester films. The method comprises the steps of :

- applying esterification or ester-interchange at below 220°C to a reaction mixture of
 - an acid component selected from the group consisting of succinic acid, succinic anhydride and succinic acid ester,
 - 1,4-butanediol as a diol component,
 - 2,2-dimethyl-1,3-propanediol of 1 to 30% by mole based on the mole of the acid component,
 - at least one multifunctional compound of 0.01 to 1% by mole based on the mole of the acid component, said multifunctional compound having at least three functional groups - identical or different - selected from hydroxy and carboxy groups ;
- polycondensing the oligomer into an aliphatic copolyester at a temperature of 240 to 260°C under reduced pressure of not more than 133.3 Pa (1 mmHg) in the presence of a catalyst ; and
- melt-extruding the aliphatic copolyester using T die.

Improved in draw ratio, the aliphatic copolyester film provided by the method can be applied to various applications, such as films, bottles, glass fiber-reinforced plastics, adhesives, paints.

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BACKGROUND OF THE INVENTION

Field of the invention

5 The present invention relates, in general, to a novel method for producing films with an aliphatic copolyester and, more particularly, to an improvement in the draw ratio of the films along with the method.

Description of the Prior Art

10 Aromatic polyesters, especially polyethylene terephthalate, are superior in physical and chemical properties and are widely used to make various applications, such as films, bottles, glass fiber-reinforced plastics, adhesives, paints and the like.

In contrast, aliphatic polyesters, although used in the forms of paint or adhesive, lack of processability, especially moldability to film. In addition, it is difficult to derive desired melt viscosity and melt strength therefrom. Furthermore, the films of aliphatic polyester, if formed, are poor in mechanical physical properties. That is to say, when aliphatic compounds are employed as the dicarboxylic acid and glycol components for polyester, the polyester, even if obtained by polycondensation after esterification or ester-interchange, is not endowed with enough melt viscosity or melt strength to be formed or processed into a film. Although it is formed and processed into a film, the final product is very inferior in workability and mechanical physical properties.

20 In order to improve the mechanical physical properties and melt strength, mainly used is a method of increasing the molecular weight thereof. In this method, however, it is of importance to appropriately control the increase of the molecular weight because too large molecular weight of the polyester may cause to raise the melt viscosity overly, which in turn results in difficulty in passing through an extruder on processing.

25 With regard to the melt strength of a polymer, it chiefly depends on the elasticity of a polymer melt. Exemplary factors affecting the elasticity include the distribution of molecular weight, the extent of branch, the kind and amount of additives. As the molecular weight is large, as the extent of branch is high and as the entanglement of polymer melt is serious, the elasticity becomes enhanced. In case of polyester, full well is it known that stearic acid, or talc or silica particle brings the melt strength into effect.

30 In addition, crystallization rate is another factor having great influence on the moldability of a polymer. The crystallization rate and crystallinity of a polymer can be controlled according to a processing method and thus, it also is of importance.

35 Japanese Patent Laid-Open Publication Nos. Heisei 4-189822 and 4-189823 disclose methods for producing polymers with enhanced melt viscosity and melt strength in which aliphatic dicarboxylic acids and aliphatic divalent glycols are subjected to esterification and polycondensation and then added with isocyanate compounds, to increase the molecular weights of the polymers. However, these methods are uneconomical because additional isocyanate compound are used. Besides, the separate addition process causes complexity and difficulty in operating the method.

SUMMARY OF THE INVENTION

40 Therefore, it is an object of the present invention to provide an aliphatic copolyester superior in melt viscosity and melt strength.

It is an object of the present invention to provide an aliphatic copolyester superior in draw ratio.

45 It is a further object of the present invention to provide a method for producing an aliphatic copolyester film, capable of improving physical properties of the film.

In accordance with the present invention, the above objects can be accomplished by a provision of a method for the production of aliphatic copolyester films, comprising the steps of: applying esterification or ester-interchange to a reaction mixture of an acid component selected from the group consisting of succinic acid, succinic anhydride and succinic acid ester, 1,4-butanediol as a diol component, 2,2-dimethyl-1,3-propanediol of 1 to 30% by mole based on the mole of the acid component, at least one multifunctional compound of 0.01 to 1% by mole based on the mole of the acid component, said multifunctional compound having at least three functional groups - identical or different - selected from hydroxy and carboxy groups at below 220°C, so as to give an oligomer mixture; polycondensing the oligomer into an aliphatic copolyester at a temperature of 240 to 260°C under reduced pressure of not more than 133.3 Pa (1 mmHg) in the presence of a catalyst; and melt-extruding the aliphatic copolyester using T die.

55 These and other objects and advantages of the present invention will become more apparent as the following description proceeds

DETAILED DESCRIPTION OF THE INVENTION

The aliphatic copolyesters provided by the present invention comprise composition consisting essentially of aliphatic dicarboxylic acids, diols, multifunctional compounds, and monomers to control crystallinity.

5 As a main component of the aliphatic copolyester of the present invention, an aliphatic dicarboxylic acid is selected from the group consisting of succinic acid, succinic anhydride and succinic acid ester. Preferred succinic acid ester used in the present invention includes dimethyl succinate, diethyl succinate, dipropyl succinate, dibutyl succinate, dioctyl succinate and the like.

The diol, another main component used in the copolyesters of the present invention, is 1,4-butanediol.

10 In view of the physical properties and color of the polymer, it is advantageous that the mole ratio of the dicarboxylic acid to the 1,4-butanediol is in a range of approximately 1:1 to 1:2 and preferably 1:1.2 to 1.7.

For a compound to control the crystallinity, 2,2-dimethyl-1,3-propanediol is used in the present invention. This compound is efficient to lower the crystallization rate because of its bulky side chain, $-\text{CH}_3$ group attached.

15 This crystallinity-controlling compound is added in amounts ranging from 1 to 30 % by mole based on the mole of the dicarboxylic acid, and more preferably 1 to 25 % by mole. For example, if the amount of 2,2-dimethyl-1,3-propanediol exceeds 30 % by mole, the copolyesters produced are overly reinforced with the characteristics of elastomer, so that they are insufficient for the blown film or for blow molding. On the other hand, if the compound is used below 1 % by mole, the addition thereof is brought into little effect.

20 For the at least multifunctional compound used in the present invention, the functional groups, which are identical or different, are hydroxy or carboxy. Preferred at least multifunctional compounds include trimethylol propane, trimethylol ethane, glycerine, pentaerythritol, dipentaerythritol, tris(2-hydroxyethyl) isocyanurate, trimellitic acid, trimellitic anhydride, benzene tetracarboxylic acid, benzene tetracarboxylic anhydride. By virtue of the copolymeric reaction of the multifunctional compound, the resulting polymers are remarkably increased in molecular weight and hence greatly improved in melt viscosity and melt strength.

25 It is critical that the at least multifunctional compounds are copolymerized in an amount of 0.01 to 1 % by mole based on the mole of the dicarboxylic acid used. For example, if they are copolymerized in amounts exceeding 1 % by mole, the polymerization reaction is completed in short times, so as to obtain high molecular weight polymers but the degree of crosslinking is rapidly raised, which leads to the formation of gel, unsuitable polymeric state to be molded. On the other hand, if the at least multifunctional compounds are used in an amount of less than 0.01 % by mole, the addition thereof is brought into no or little effect.

30 According to the present invention, an aliphatic copolyester film is produced by applying esterification or ester-interchange to a reaction mixture of an acid component selected from the group consisting of succinic acid, succinic anhydride and succinic acid ester, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol 1 to 30 % by mole based on the mole of the acid component, at least a multifunctional compound of 0.01 to 1 % by mole based on the mole of the acid component at below 220 °C, so as to give an oligomer mixture, polycondensing the oligomer into an aliphatic copolyester at a temperature of 240 to 260 °C under reduced pressure of not more than 133.3 Pa (1 mmHg) in the presence of a catalyst, and melt-extruding the aliphatic copolyester using T die.

40 In order to minimize the formation of by-product and thermal decomposition, the esterification or ester interchange is carried out at reaction temperatures below 220 °C.

45 As to the catalyst used in the polycondensation, tin-containing compounds or titan-containing compounds are useful. As the tin-containing compounds, there are exemplified tin oxides, such as stannous oxide and stannic oxide, tin halides such as stannous chloride and stannic chloride, stannous sulfides, and organic tin compounds such as monobutyl tin oxide, dibutyl tin oxide, monobutylhydroxy tin oxide, dibutyl tin dichloride, tetraphenyl tin and tetrabutyl tin. As the titan-containing compound, tetrabutyl titanate, tetramethyl titanate, tetraisopropyl titanate, or tetra(2-ethylhexyl) titanate may be used. The amount of the catalyst used in the polycondensation is preferably on the order of approximately 1.0×10^{-4} to 1.0×10^{-3} mole per gram of oligomer obtained in the esterification or ester interchange. For example, if too much catalyst is used, discoloration of polymer takes place. On the other hand, if too little catalyst is used, the reaction rate becomes slow.

50 Besides the above-mentioned components, the copolyesters according to the present invention may include other additives including a thermal stabilizer and a nucleating agent.

55 With regard to the thermal stabilizer, useful is a phosphorous-containing compound, such as phosphoric acid, monomethyl phosphoric acid, trimethyl phosphoric acid, tributyl phosphoric acid, trioctyl phosphoric acid, monophenyl phosphoric acid, triphenyl phosphoric acid and derivatives thereof, phosphorous acid, triphenyl phosphorous acid, trimethyl phosphorous acid and derivatives thereof, and phenyl phosphonic acid, among which phosphoric acid, trimethyl phosphoric acid and triphenyl phosphoric acid are excellent. Besides, Irganox 1010, Irganox 1222 and Irganox 168, all of which are trade names commercially available from Ciba-Gigley company. When used as a thermal stabilizer, the phosphorous-containing compound is added in an amount of ap-

proximately 1.0×10^{-6} to approximately 1.0×10^{-3} mole per gram of the oligomer obtained by esterification or ester interchange.

For a nucleating agent, titan dioxide, talc, sodium sulfide, or silicon dioxide may be used.

For the purpose of high molecular weight copolyester with a high melt viscosity and melt strength, it is important to polycondense the oligomer at high vacuum states and efficient at reaction temperatures ranging from approximately 240 to approximately 260 °C. For example, if the reaction temperature is below 240 °C, the reaction rate in the polycondensation is very slow, so that a polymer with a desired molecular weight is difficult to obtain. On the other hand, if the reaction temperature exceeds 260 °C, pyrolysis takes place so extremely that the color or physical properties of the polymer become inferior.

Melt strength of the copolyesters of the present invention is determined according to ASTM D 3835 by extruding the molten polymer downward through a die 0.1 inch in diameter and 0.25 inches long at a shear rate of 20 second⁻¹ using as Instron rheometer and allowing the extrudate to fall freely. The diameter of the end of a six inch length of extrudate (measured from the exit face of the die) is measured. The percent melt strength is determined from the formula:

$$\text{Melt Strength} = \frac{D_{\text{MELT}} - D_{\text{DIE}}}{D_{\text{DIE}}} \times 100$$

wherein

D_{DIE} is the diameter of the rheometer (=0.1 inch),

D_{MELT} is the diameter, in inches, of the extrudate supporting a six inch length of extrudate.

It is known that there is a close correlation between percent melt strength and suitability for extrusion blow-molding and the copolyesters having a melt strength percent of at least 10 are used to extrusion blow-mold articles (U.S. Patent No. 4,983,711). The aliphatic copolyesters provided by the present invention have a melt strength of 10 or greater.

The preferred embodiment of the present invention will now be further described with reference to specific examples.

EXAMPLE 1

Into a reactor equipped with a stirrer and a condenser, 136 g (1.5108 mole) of 1,4-butane diol (hereinafter referred to as "BD"), 12 g (0.1152 mole) of 2,2-dimethyl-1,3-propane diol (hereinafter referred to as "NPG"), 137 g (1.1601 mole) of succinic acid (hereinafter referred to as "SA"), 0.7 g (0.0058 mole) of trimethylol ethane (hereinafter referred to as "TME"), and 1.02 g (0.0003 mole) of a slurry of catalyst (hereinafter referred to as "CAT") which had been obtained by stirring a mixture of 90 % by weight of BD and 10 % by weight of tetrabutyl titanate for 3 hours were charged.

The reactor was heated from room temperature to 120 °C over 40 minutes and then to 210 °C over 120 minutes with stirring, so as to react the contents. Thereafter, water, the by-product, was completely drained through into the condenser.

Over 45 minutes, the pressure within the reactor was slowly reduced into 0.5 mmHg and the temperature was raised up to 245 °C, simultaneously with stirring for 120 minutes. After the stirring, nitrogen gas was charged into the reactor and a high pressure was applied, so as to give an aliphatic copolyester resin.

The resin obtained was melt at 180 °C through an extruder and then formed into a compressed film through a T die, which was subsequently drawn in 4 x 3 times at 85 °C, so as to give a transparent film with a thickness of 25 to 30 μm.

Physical properties for the resin and film were measured as follows:

- Intrinsic Viscosity: polymer is dissolved in ortho-chlorophenol 30 °C and then its intrinsic viscosity is measured using a capillary viscometer.
- Crystallization Melting Point: a differential thermal analyzer is used (°C).
- Melt Viscosity: using a rheometer commercially available from Rheometric Company under a trade name of RDS-7700, at 190 °C and at 10³sec⁻¹.
- Weight Average Molecular weight using gel penetration chromatography.
- Tensile Strength: according to ASTM D 412 (kg/cm²).
- Elongation at Rupture: according to ASTM D 412 (%).

The results are given as shown in the following Table 2.

EXAMPLES 2 TO 10 AND COMPARATIVE EXAMPLES 1 TO 3

Aliphatic copolyesters and films were prepared in a manner similar to that of Example 1, except that the

amount of NPG and the amount and kind of the multifunctional compound were employed as given in the following Table 1.

Physical properties also were measured as stated in Example 1 and the results are given as shown in the following Table 2.

EXAMPLES 11 AND 12 AND COMPARATIVE EXAMPLE 4

Into a reactor equipped with a stirrer and a condenser, such components as are given in the following Table 3 were charged.

The reactor was heated from room temperature to 120 °C over 40 minutes and then to 210 °C over 120 minutes with stirring, so as to react the contents. Thereafter, methanol, the by-product, was completely drained through into the condenser.

Over 45 minutes, the pressure within the reactor was slowly reduced into 0.5 mmHg and the temperature was raised upto 248 °C, simultaneously with stirring for 120 minutes. After the stirring, nitrogen gas was charged into the reactor and a high pressure was applied, so as to give an aliphatic copolyester resin.

An aliphatic copolyester film was produced in a manner similar to that of Example 1.

The aliphatic copolyester and film was tested for its physical properties and the results are given as shown in Table 4.

EXAMPLES 13 AND 14 AND COMPARATIVE EXAMPLE 5

Into a reactor equipped with a stirrer and a condenser, such components as are given in the following Table 3 were charged.

The reactor was heated from room temperature to 120 °C over 40 minutes and then to 210 °C over 120 minutes with stirring, so as to react the contents. Thereafter, ethanol, the by-product, was completely drained through into the condenser.

Over 45 minutes, the pressure within the reactor was slowly reduced into 0.5 mmHg and the temperature was raised upto 252 °C, simultaneously with stirring for 120 minutes. After the stirring, nitrogen gas was charged into the reactor and a high pressure was applied, so as to give an aliphatic copolyester.

An aliphatic copolyester film was produced in a manner similar to that of Example 1.

The aliphatic copolyester and film was tested for its physical properties and the results are given as shown in Table 4.

EXAMPLES 15 AND 16

Into a reactor equipped with a stirrer and a condenser, such components as are given in the following Table 3 were charged.

The reactor was heated from room temperature to 120 °C over 40 minutes and then to 210 °C over 120 minutes with stirring, so as to react the contents. Thereafter, propanol, the by-product, was completely drained through into the condenser.

Over 45 minutes, the pressure within the reactor was slowly reduced into 0.5 mmHg and the temperature was raised upto 251 °C, simultaneously with stirring for 120 minutes. After the stirring, nitrogen gas was charged into the reactor and a high pressure was applied, so as to give an aliphatic copolyester.

An aliphatic copolyester film was produced in a manner similar to that of Example 1.

The aliphatic copolyester and film was tested for its physical properties and the results are given as shown in Table 4.

EXAMPLES 17

Into a reactor equipped with a stirrer and a condenser, such components as are given in the following Table 3 were charged.

The reactor was heated from room temperature to 120 °C over 40 minutes and then to 210 °C over 120 minutes with stirring, so as to react the contents. Thereafter, butanol, the by-product, was completely drained through into the condenser.

Over 45 minutes, the pressure within the reactor was slowly reduced into 0.5 mmHg and the temperature was raised upto 246 °C, simultaneously with stirring for 120 minutes. After the stirring, nitrogen gas was charged into the reactor and a high pressure was applied, so as to give an aliphatic copolyester.

An aliphatic copolyester film was produced in a manner similar to that of Example 1.

The aliphatic copolyester and film was tested for its physical properties and the results are given as shown in Table 4.

Table 1

Example No.	Composition										
	SA	BD	NGP	TME	TMP	TMA	TMAN	PNT	DPNT	GLY	CAT
1	137	136	12	0.7	-	-	-	-	-	-	1.02
C1	137	136	-	-	-	-	-	-	-	-	1.02
C2	137	136	12	-	-	-	-	-	-	-	1.02
2	137	136	12	-	0.8	-	-	-	-	-	1.02
3	137	136	12	-	-	1.2	-	-	-	-	1.02
4	137	136	12	-	-	-	1.1	-	-	-	1.02
5	137	136	12	-	-	-	-	0.8	-	-	1.02
6	137	136	12	-	-	-	-	-	1.1	-	1.02
7	137	136	12	-	-	-	-	-	-	0.6	1.02
C3	137	136	36,3	0.7	-	-	-	-	-	-	1.02
8	137	136	8	-	-	0.7	-	-	-	-	1.02
9	137	136	15	-	-	-	-	0.8	-	-	1.02
10	137	136	10	-	-	-	-	-	-	0.5	1.02

* SA : succinic acid BD : 1,4-butanediol
 NGP : 2,2-dimethyl-1,3-propanediol,
 TME : trimethylol ethane
 TMP : trimethylol propane TMA : trimellitic acid
 TMAN : trimellitic anhydride, PNT : pentaerythritol
 DPNT : dipentaerythritol, GLY : glycerine
 CAT : catalyst slurry

Table 2

Example	Physical Properties					
	No.	MP(°C)	IV(dl/g)	MV(poise)	Mw	UST (kg/cm ²)
	1	105.7	1.426	2,700	235,000	650
	C1	114.1	1.178	1,200	78,000	#
	C2	105.6	1.182	1,300	115,000	300
	2	106.3	1.435	2,500	264,000	590
	3	107.4	1.470	2,900	221,000	580
	4	106.6	1.501	2,700	218,000	620
	5	106.0	1.382	2,900	268,000	635
	6	107.4	1.424	3,100	215,000	670
	7	105.8	1.395	2,600	249,000	640
	C3	78.4	1.388	2,900	238,000	540
	8	110.5	1.483	2,500	219,000	560
	9	102.5	1.406	2,700	222,000	635
	10	108.3	1.422	3,000	215,000	670

* MP : melting point, IV : intrinsic viscosity

MV : melt viscosity, Mw : molecular weight

UST : tensile strength of film,

Elon : elongation ratio at break

#: heterogeneously elongation

Table 3

Example No.	Composition										
	DMS	DES	DPS	DBS	BD	NGP	TME	TMA	PNT	CAT	DPNT
11	170	-	-	-	136	10	0.6	-	-	-	1.02
12	170	-	-	-	136	7.0	-	-	0.6	-	1.02
C4	170	-	-	-	136	36.3	-	-	-	-	1.02
13	-	202	-	-	136	10.0	-	-	-	0.8	1.02
14	-	202	-	-	136	13.0	-	0.6	-	-	1.22
C5	-	202	-	-	136	36.3	-	-	-	-	1.22
15	-	-	235	-	136	14.0	-	0.5	-	-	0.95
16	-	-	235	-	136	11.0	-	-	0.9	-	1.02
17	-	-	-	267	136	12.0	0.5	-	-	-	1.05

* DMS : dimethyl succinate, DES : diethyl succinate
 DPS : dipropyl succinate, DBS : dibutyl succinate
 BD : 1,4-dibutane diol,
 NGP : 2,2-dimethyl-1,3-propanediol,
 TME : trimethylol ethane TMA : trimellitic acid
 PNT : pentaerythritol DPNT : dipentaerythritol
 CAT : catalyst slurry

Tabl 4

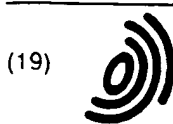
Physical Prop rties							
Exempl No.	MP(°C)	IV(dl/g)	MV(poise)	Mw	UST (kg/cm ²)	Elon (%)	
11	105.7	1.422	2.500	214,000	670	230	
12	109.2	1.478	2.600	241,000	555	210	
C4	78.3	1.205	1,200	114,000	280	350	
13	106.1	1.442	2,900	232,000	560	190	
14	103.4	1.397	3,100	244,000	640	185	
C5	78.1	1.187	1,300	125,000	260	340	
15	102.7	1.406	2,800	221,000	615	200	
16	104.5	1.425	2,700	232,000	560	185	
17	105.0	1.433	2,000	253,000	660	190	

Other features, advantages and embodiments of the invention disclosed herein will be readily apparent to those exercising ordinary skill after reading the foregoing disclosures. In this regard, while specific embodiments of the invention have been described in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as described and claimed.

Claims

1. A method of production of aliphatic polyester films, comprising the steps of:
 - applying esterification or ester-interchange at below 220°C to a reaction mixture of
 - an acid component selected from the group consisting of succinic acid, succinic anhydride and succinic acid ester,
 - 1,4-butanediol as a diol component,
 - 2,2-dimethyl-1,3-propanediol of 1 to 30% by mole based on the mole of the acid component,
 - at least one multifunctional compound of 0.01 to 1% by mole based on the mole of the acid component, said multifunctional compound having at least three functional groups - identical or different - selected from hydroxy and carboxy groups;
 - polycondensing the oligomer into an aliphatic copolyester at a temperature of 240 to 260°C under reduced pressure of not more than 133.3 Pa (1 mmHg) in the presence of a catalyst; and
 - melt-extruding the aliphatic copolyester using T die.
2. A method of production of aliphatic copolyester films according to claim 1, wherein the multifunctional compound(s) is (are) selected from the group consisting of trimellitic acid, trimellitic anhydride, trimethylol ethane, trimethylol propane, pentaerythritol, dipentaerythritol and glycerine.
3. A method of production of aliphatic copolyester films according to claim 1 or 2, wherein succinic acid compound is selected from the group consisting of dimethyl succinate, diethyl succinate, dipropyl succinate and dibutyl succinate.

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(54) Method for the production of aliphatic copolyester films

(57) There is disclosed a method for the production of aliphatic copolyester films. The method comprises the steps of:

applying esterification or ester-interchange at below 220°C to a reaction mixture of

- an acid component selected from the group consisting of succinic acid, succinic anhydride and succinic acid ester.
- 1,4-butanediol as a diol component.
- 2,2-dimethyl-1,3-propanediol of 1 to 30% by mole based on the mole of the acid component.
- at least one multifunctional compound of 0.01 to 1%

by mole based on the mole of the acid component .
said multifunctional compound having at least three functional groups - identical or different - selected from hydroxy and carboxy groups:

polycondensing the oligomer into an aliphatic copolyester at a temperature of 240 to 260°C under reduced pressure of not more than 133.3 Pa (1 mmHg) in the presence of a catalyst; and

melt-extruding the aliphatic copolyester using T die.
Improved in draw ratio, the aliphatic copolyester film provided by the method can be applied to various applications, such as films, bottles, glass fiber-reinforced plastics, adhesives, paints.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 40 2464

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,A	EP 0 569 143 A (SHOWA HIGHPOLYMER CO., LTD.) * claims 1,9-12; example 8 *	1-3	C08G63/16 C08G63/20 C08J5/18
A	EP 0 015 431 A (BAYER AG) * page 5, line 1 - line 25; claims 1-3 *	1-3	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08G C08J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 May 1997	Examiner Decocker, L
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date U : document cited in the application L : document cited for other reasons id : member of the same patent family, corresponding document</p>			

EP 0 650 994 A3 (P) (CO)